Original Research Article

Potentiality of Alcoholic Purification of Abu-Zaabal Impure Phosphoric Acid for Selective Ion Exchange Recovery of Uranium

Abstract

A suggested procedure was studied for recovering of uranium selectively from the Abu Zaabal impure phosphoric acid assaying about 46% P_2O_5 and about 3% iron. This procedure involves the application of an alcoholic precipitation step for most impurities by using isopropyl alcohol and cationic resin where uranium was kept in the acid phase by a prior oxidation step. After distillation of alcohol for recycling, the uranium in the purified phosphoric acid was properly reduced to U^{+4} and recovered via the Chinese cation exchange resin namely; amino phosphonic (D4O4). Displacing Fe^{+2} from the resin , washing the resin with aqueous ammonia , eluting the resin with carbonate – bicarbonate solution and precipitating uranium from the elute as UO_3-$2H_2O$.

Key words : Recovering Uranium – Abu Zaabal – Alcoholic precipitation – Amino phosphonic resin D4O4

1. Introduction

Generally, uranium is found in natural phosphate in the concentrations ranged from 0.005% - 0.02 %(**Alonso et al., 1997**) . It was reported that 6.34 million tones of uranium exist in phosphate throughout the world (**Streat and Naden 1984**). Besides the phosphorous value, phosphate rocks whose world's resources are estimated to be about 18000 million tons can indeed be considered as a secondary resource for some interesting metal values uranium and rare earth elements .

Technologically, U extraction from wet process phosphoric acid (WPPA) has been developed by the solvent extraction technique using some organophosphene compounds up to the commercial scale. **Wetering and Janssen** (1985) have also studied a new and considerably cheaper process (precipitation method) and have even claimed that it would be considerably cheaper in a manner to replace the still exclusively based solvent extraction expensive methods. This is due to the pre – purification step of phosphoric acid which is necessary to assist phase separation besides the subsequent acid treatment step in order to prevent the attack of the Auber lining of the phosphoric acid evaporation equipment.

Several other methods for uranium recovery from phosphoric acid have been proposed e.g. U precipitation through replacement of calcium in the calcium sulfate hemi hydrate or dehydrate (gypsum) or else via liquid emulsion membranes **(ElHazek and ElSayed, 1995)**. However, the latter still too expensive as in the case with solvent extraction. In this regard, it has to be also indicated that solvent extraction of U cannot be applied in the direct production high concentration acid >45 % P_2O_5 .After this brief review, it has to be indicated that **Wetreing and Janssen(1985**) published a new process o recover U after prior reduction of U^{6+} to U^{4+} using 0.15 g iron powder for 100g phosphoric acid during 30 min for low and 15 min for high concentration acid. From both high and low P_2O_5 concentration of phosphoric acid Via its direct precipitation, this has been possible by addition of an organic liquid such as acetone as the dispersion agent in combination with a precipitating agent preferably NH_4F or other precipitating acid that would be added during the continued mixing of the iron powder. In the meantime, this procedure would result in co – precipitation of Y, REEs as well as V. After dissolution of the obtained precipitate ≥ 0.25 H_2SO_4, U can be extracted with Dowex 1, 100 – 200 mesh size exchange resin in the H_2SO_4 form and elution with nitric acid.

Actually, the use of solid ion exchangers for U recovery from WPPA has become attractive due to some potential advantages with respect to SX process. This is nearly due to the fact that this technique is relatively of lower cost is less affected by the concentration of the acid and by temperature. In addition, the acid would not be contaminated with organic solvent and does not need a pre- treatment. Several authors have indeed studied this alternative specially after the development of the superior chelating resins containing hydroxyl- phosphonic or amino – phosphonic functional groups that adsorb U in the tetravalent state. Ion exchange processes using the solvent-containing polymeric resins have been also tested (**Gonzalez-Luque, 1982, Ketzinel et al., 1985**). The aminomethylphosphonic resin Duolite ES 467 was found selective for the recovery of U from wet-process phosphoric acid (**Gonzalez-Luque and Streat, 1983a, 1983b, 1984). Kabay et al., 1998,** published a study on the application of several chelating resins containing phosphonic or phosphinic groups to the recovery of U from phosphoric acid solutions. It was shown that the aminomethyl phosphonic resin Purolite S940 gives a promising sorption/elution behaviour working in small column extractions of U from phosphoric acid solutions.The aminomethylphosphonic resin duolite Es467 was found selective for the recovery of U from wet. Process phosphoric acid. (**Volkmous, 1989, Singh, et al, 2001, and Soldenhoff, et al, 2009).** Commercial aminophosphonic resins of Na – type as supplied involve Lewatit TP 260 (2.3 eq/L), Purolite S 940 (2.0 eq/L), Amberlite IRC 747 (1.75 eq/L) and Duolite C 467 (1.0 eq/L). According to **Areski, ,(2013). and William (2015)** the use of solid ion exchangers for the recovery of uranium from phosphoric acid has become attractive in the last few years. The development of more selective resins and the recent successful installation of several plants using continuous – exchange (CIX) system have promoted interest in this technology.

The present work has thus been mainly concerned with the recovery of U from the concentrated WPPA phosphoric acid produced by Abu Zaabal fertilizers and chemical Co. . For this purpose the above mentioned precipitation procedure of Watering and Janssen (1985) was used however, due to the relatively high iron The procedure involved an alcoholic precipitation step of most impurities mainly iron using isopropyl alcohol (IPA) where uranium was kept in the acid phase by a prior oxidation step. After distillation of alcohol for recycling, the uranium in the purified phosphoric acid was properly reduced and recovered via the Chinese cation exchange amino phosphonic resin (D4O4) . The latter is a chelating resin in the big pure styrene cross linking copolymerization – two vinyl sphere introduce amino acid chelating genes. It can finish the exchange – adsorption capabilities no matter what pH value. This product has the large capacity of exchange 2.4 mmol/L, exchange speed, good mechanical strength,ect.. It was shown that the amino phosphonic resin D4O4 gives a promising sorption/elution behaviour working in small column extraction of U from phosphonic acid solution. .

2-Experimental

2.1,Materials

2.1.1. Chemicals and reagents

In the present work the applied miscible solvent IPA has been supplied by Fine Chem. Ltd, India. The other chemicals and reagents used for preparing the working phosphoric acid besides those used for chemical analysis have mostly been of analytical grade.

The working crude H_3PO_4 acid of Abu Zaable Company produced through sulphuric acid route .The chemical analysis of the acid shown that it contains many undesirable elements.(**AbdElfattah,N.A.2015**). In order to improve the purity of Abu Zaable concentrated phosphoric acid humic materials, fluoride and sulphates must be decrease. Table (1) show the composition of Abu Zaabal crude phosphoric acid.

Table(1): Composition of the Abu Zaabal crude H_3PO_4 acid.

Component	Wt %	Component	ppm
P_2O_5	48.2	U	74
SO_4	2.60	Ca	54
Fe	2.73	Cd	9.7
F	0.48	V	260
Mn	0.155	REEs	560

2.2. Methods

2. 2.1. Analytical procedures

Several analytical procedure were performed in order to determine the purity and the concentration of the impure phosphoric acid. The cations in this medium were detected with Atomic Absorption Spectroscopy, GBC 932 AA. Phosphoric acid concentration was detected with acid base titration against 0.1 N NaOH while the precipitated P_2O_5 was detected using Spectrophotometer method**.**

2.2.1.1. U Control Analysis

For uranium analysis in the different working experimental stream solutions, the oxidimetric titration method using ammonium metavanadate has been applied. For this purpose, a prior uranium reduction was performed by $(NH4)_2Fe(SO_4)_2$ in the presence of diphenylamine sulfonate indicator until it changes to a slightly violet colour(**Davies and Gray, 1964)** U (g/l) = T.V1 / V. 1000 where V1: volume taken of NH_4VO_3 solution (ml)

V: sample volume (ml) and T: concentration of NH_4VO_3 to U (g/ml)

2.2.1.2. Control analysis of REEs

For the REEs analysis in the different working experimental stream solutions, the REEs content was spectrophotometically determined by Arsenazo III as a complexing agent and the absorbance was measured at 650 nm against proper standard solutions **(Marezenko, 1986)** using a Lambada UV/VIS spectrophotometer (Perkin-Elmer, USA).

2.2.1.3. Determination of sulfate

In the present work determination of soluble sulphate was performed by using turbid metric method using $BaCl_2$. In this method, sulphate is precipitated as $BaSO_4$, and the resultant turbidity was compared with that produced in a series of chemical standards of known concentrations according to sulphate calibration curve**.**

2.2.1.4 Determination of Fluoride

Fluoride ion concentration in the working and purified phosphoric acid was measured by the ion selective electrode technique where 0.05 ml of sample was taken with 0.45ml of sodium acetate tri-hydrate to adjust the pH of the sample at 5.0. This was followed by the addition of the TISAB to adjust the ionic strength of the solution and which was then diluted and made up to volume with bi-distilled water to 500 ml in a plastic flask. From the latter, 50 ml was taken and its fluoride ion concentration was measured by the ion selective electrode (Jenway, UK).

2.2.2. Recovery procedures

2. 2 .2.1 Commercial acid pre-treatment

2.2.2.1.1. Removal of humic matters

In this regard, it was found interesting to subject the provided acid to a pre-treatment procedure. Humus matters tend to dissolve with the organic phase as the base, like dissolve like. So, the commercial phosphoric acid has involved its clarification using clay (12g for 1L, 1580gm crude WPPA 48% P_2O_5). This is done at room temperature with 400 rpm mixing speed and half an hour mixing time. After clay treatment the commercial acid was then subjected to sulphate precipitation.

2.2.2.1.2. Sulphate precipitation

Using 42.6 gm calcium carbonate for precipitating the excess sulphuric acid in 1580gm crude phosphoric acid . The precipitation of sulphate occurred while mixing and keeping the working acid at more than 600 mv using 0.4ml H_2O_2 in order to prevent the partial precipitation of uranium with calcium sulphate formation.

$$H_2SO_4 + CaCO_3 \longrightarrow CaSO_4 + H_2O$$

This was then followed by defluorination of the crude acid.

2.2.2.1.3. Defluorination

Precipitation of 0.48% fluorine from 1580gm crude phosphoric acid Using 3.8gm fine silica,**).** After mixing for 1 hr at 400 rpm, the formed fluosilicic acid was precipitated as sodium fluorosilicate by using 4.5 gm sodium carbonate, viz:

$$6HF + SiO_2 \longrightarrow H_2SiF_6 + 2\,H_2O$$

$$H_2SiF_6 + Na_2CO_3 \longrightarrow Na_2SiF_6 + CO_2 + H_2O$$

Coagulation was performed using 5 ml of 0.2 % polyacrylamide solution which make enhancement of colloidal solid precipitation.

2.2.2.1.4. Oxidation process

The treated acid free from either fluoride and sulphate have been then subjected to oxidation process by using H_2O_2 to convert U^{+4} to U^{+6}. The purpose was prevent its precipitation with the impurities during further purification by using IPA.

2.2.2.1.5.Alcoholic and cationic resin purification of H_3PO_4

Further purification of H_3PO_4 have been studied to precipitate the present impurities in the working acid such as sulphate, heavy metals and others. The purpose was to obtain the optimum precipitation conditions. The studied factors such as the acid - solvent ratio, precipitating agent - acid ratio and the redox potential of the acid. IPA was used as a miscible solvent while ammonium was used as a precipitating agent. After filtration the acid alcohol phase passing on cationic resin (Amberlite IR120) .

2.2.2.2. Extraction of uranium

2.2.2.2.1. Adsorption process

About 2ml of D4O4 resin was packed in a glass column whose diameter 0.25 cm. length 10 cm. The resin was then treated by 5% HCl solution and soaked for 2h in acid followed by washing and treatment by 4%NaOH and soaked for 2h. Finally 5% HCl was pour in to the column and good washing by H_2O until pH 7 followed by passing the WPA. Saturation of uranium take place after the passage of 3L (6BV)

2.2.2.2.2 Elution process

After saturation, the loaded D4O4 resin was then subjected to the elution process. This has been performed by using 30 % H_3PO_4 to remove Fe^{+2} while using ammonium carbonate for eluting of uranium.

3.RESULTS AND DISCUSSION

3.1. Purification of crude phosphoric acid

3.1.1. Composition of H_3PO_4 acid after pre-treated

In the present work the concentrated commercial phosphoric acid (50% P_2O_5), was used after removal of humic materials, fluoride and sulphate to precipitate the impurities by miscible solvent technique. Table (2) shows the analysis of the pre-treated concentrated working acid accompanied by desulfurization and defluorination as previously mentioned in the experimental part.

Table (2)The composition of the working acid 50% P_2O_5

Component	**Wt. %**	**Component**	**ppm**
P_2O_5	**50.0**	**U**	**77.0**
SO_4	**0.34**	**Ca**	**340.0**
Fe	**2.88**	**Cd**	**10.4**
F	**0.15**	**V**	**275**
Mn	**0.158**	**REEs**	**560**

From this table it could be concluded that the percent of sulfate and fluoride decreased from 2.6, and 0.48 to 0.34 and 0.15 respectively as a result for desulfurization and defluorination

3.1.2. Alcoholic purification

To separate most of the metal values and impurities, it was found convenient to subject the preliminary purified acid to a second purification step using a proper precipitant together with a water miscible solvent (isopropyl alcohol). However, in order to keep uranium soluble in the purified acid / alcohol mixture it was previously oxidized by H_2O_2.

Table (3) : Effect of addition precipitating agent on IPA quantity needed to iron precipitation and uranium kept in WPA.

Exp.NO.	**gNH_3Per/ 100gP_2O_5**	**Dispersant g/100gP_2O_5**	**State of U**	**U precipitation Efficiency%**
1	**6**	**400**	**Oxidized**	**<10**
2	**7**	**350**	**Oxidized**	**<10**
3	**8**	**300**	**Oxidized**	**<10**

From the table (3) uranium can be kept in phosphoric acid by oxidized it to hexavalent state followed by addition of precipitating agent in combination with IPA liquid for removal of iron as ammonium iron phosphate, and re concentration of valuable metals as V and REE.s

3.1.3.Composition of the working acid after precipitation

The acid after filtration consists of a mixture of IPA, uranium and some of impurity. This acid have been subjected to distillation for recovery of IPA for reused where the percent of recovery about 96%while the percent of acid recovery represents about 90%

Table (4): Analysis of the components of the partially purified phosphoric acid after IPA treatment.

Component, %		Component, ppm						
P_2O_5	Fe	F	U	Cd	Mn	Ca	V	REEs
46.2	0.088	105	74	0.3	92	38	37	52

3. 1.4.Composition of the obtained precipitant.

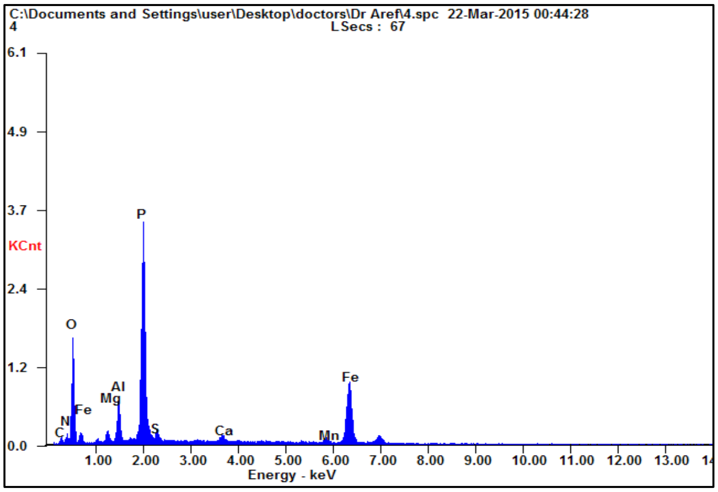
After proper filtration of the obtained precipitant and distillation of the acid / alcohol mixture, the compositions of the precipitant have been determined. The humidity was measured by drying at 120C^0 for an 2hours. The weight of the relevant precipitate was18.4g which would be analyzed for iron, cadmium, vanadium and calcium using atomic absorption spectroscopy. Fluoride is detected by ion selective electrode, table (5).

Table (5): Composition of the viscous precipitate after phosphoric acid partially purification

Component, %					Component, ppm				
P_2O_5	Fe	F	Mn	Moisture	U	Ca	Cd	V	REEs
52.2	8.8	0.24	0.565	32	5	139	27	610	1410

The precipitate obtained is considered of a high value due to containing a high concentration of vanadium, rare earths and cadmium. It is necessary to extract this metal value from the obtained metal phosphate precipitate by ion exchange or solvent extraction techniques after dissolution of the precipitate in sulphuric acid.

Fig. (1): EDAX analysis of the ammonium iron phosphate compound formed after IPA and ammonium salt addition



3.1.5.The highly purification by cationic resin

The acid before filtration contains some of associated metals as iron ,vanadium, rare earths and manganese in less amount by passing over cation resin(Amberlite IR 120) the result was important where all the cation metals adsorbed on resin except uranium which in hexavalent state table (6).

Table (6): Analysis of the components of the highly purified phosphoric acid after Amberlite IR 120 Resin treatment.

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Component, %		Component, ppm						
P_2O_5	Fe	F	U	Cd	Mn	Ca	V	REEs
46.2	0.008	105	74	0.3	2	nil	Nil	nil

3.2. Recovery of uranium

3.2.1.The loading process

The pre-treatment of WPA acid which contains uranium in hexavalent state after passing on Amberlite 120 resin have been subjected to reduction by iron powder to convert uranium to tetravalent state for passing through D4O4 resin for selective separation of uranium.

About 3L of purified acid 40% contains U and Fe 74 and 500 ppm respectively pass over 1.5 ml of D4O4 resin after treatment. The flow rate about 0.3ml /min., the acid effluent was subjected to uranium analysis every 500 ml. The result of adsorption showed that the percent of loading reach to about 75% where the first three sample after analysis of uranium proven that the loading percent 100% otherwise the percent of loading decrease in the latter three sample 75,50 and 15% respectively. After saturation and washing the resin was subjected to elution process.

Table(7): Analytical results of Abu-Zaable effluent purified WPA usingD4O4 resin(each aliquot sample Vol=500ml).

Effluent sample No. (500 ml)	Uranium assay mg/l	Uranium adsorption, %
1	Nil	100
2	Nil	100
3	Nil	100
4	18	75
5	37	50
6	54	15

3.2.2. Procedure of elution

An ion exchange column was loaded with uranium by feeding it with reduced WPA. Loading was continued until saturation of the resin. At this point, the column was loaded with 0.16g of uranium. After rinsing with water, elution with a solution of ammonium- carbonate 6%e.About 200ml of eluting agent was pass in two fraction after analysis of uranium the first fraction contain about 1000 mg/l where the second contain about 600 mg/l. The color of the solution that emerged from the column was dark brown indicating the presence of organic matter. To precipitate uranium from loaded ammonium- carbonate solution is based on evaporation of the solution until boiling where ammonia and carbon dioxide evolve, As their concentration in the mother liquor decrease until pH7 at which uranium precipitate as $UO_{3}.2H_2O$.

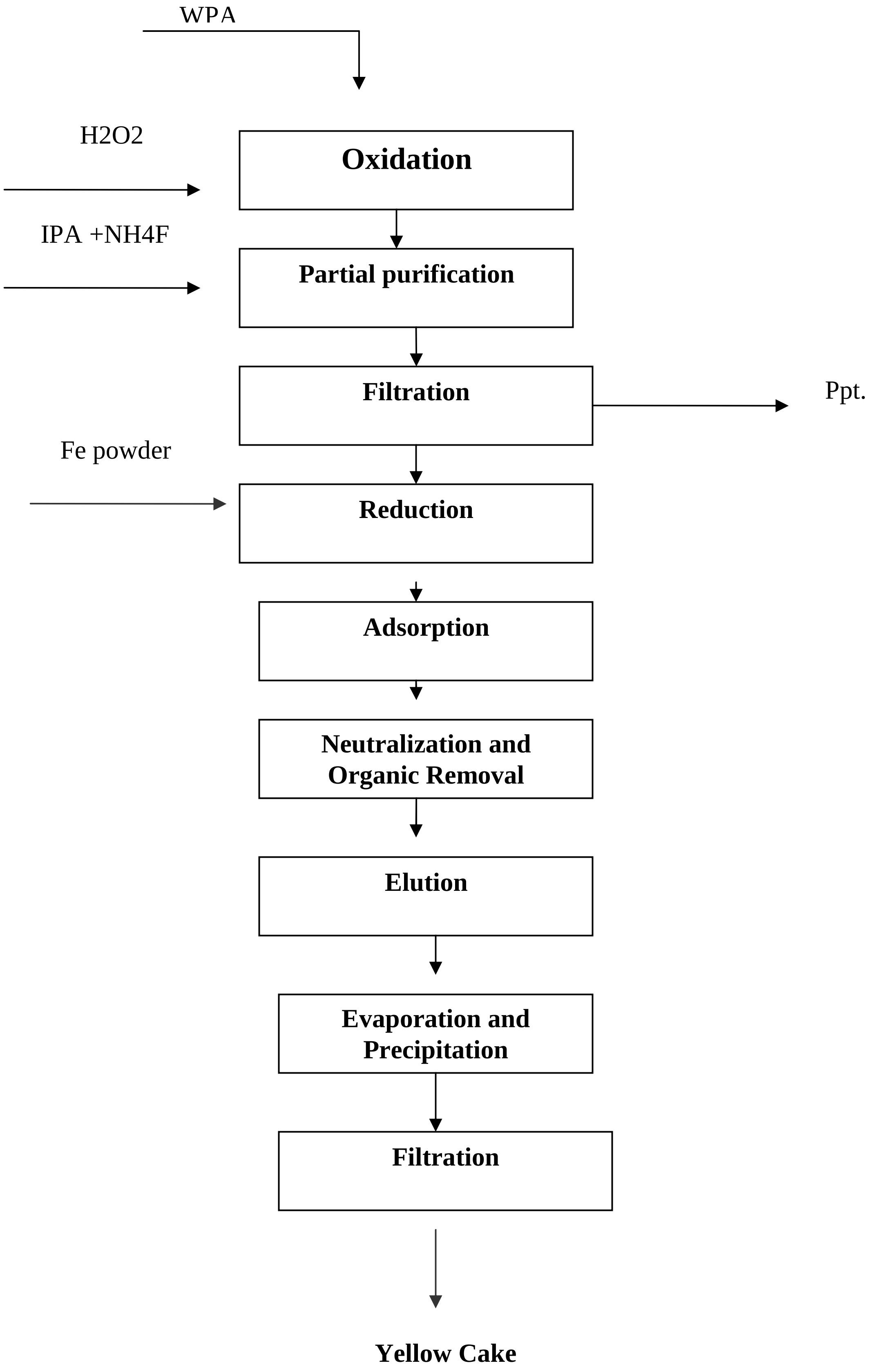

Fig. (2) : Flow Sheet for partial purification and selective separation of uranium from Egyptian wet phosphoric acid by solvent extraction and ion exchange

Conclusion

The work presents a new process integrating for partial purification and selective separation of uranium from Egyptian WPA by miscible solvent and D4O4 cation exchange linked by active aminophosphonic group as follow

i- Subjecting crude acid after deflorination and desulfurization processes to oxidation treatment thereby to oxidized uranium to hexavalent state.

ii- contacting the so- oxidized acid to purification by IPA solvent and ammonium salts precipitation agent.

iii-Subjecting the acid before recycling IPA for passing over cationic resin followed by reduction.

iv- Contacting the so – reduced acid with a cation exchange resin D4O4 to load the latter with tetravalent uranium.

v- Thereafter subjecting the loaded cation exchange resin to treatment with aqueous ammonia thereby to neutralize free acid group, remove any organic matter.

vi- Eluting the neutralized, loaded D4O4 resin with an aqueous solution of a mixture of carbonate and bicarbonate of ammonium

vii- Precipitating a uranium product from the resulting eluate .

Disclaimer:

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